

Sensitive Detection and Identification of Isovanillin Aerosol Particles at the pg/cm^3 Mass Concentration Level Using Raman Spectroscopy*

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A compact Raman spectroscopy system with high sensitivity to chemical aerosols has been developed. This system has been used to detect isovanillin aerosols with mass concentration of $12 \text{ pg}/\text{cm}^3$ in a 15 s signal integration period with a signal-to-noise ratio of 32. We believe this represents the lowest chemical aerosol concentration and signal integration period product ever reported for a Raman spectroscopy system. The Raman system includes (i) a 10 W, 532-nm cw laser, (ii) an aerosol flow cell, (iii) a 60x aerosol concentrator, (iv) an f/1.8 Raman spectrometer with a spectral range of $400\text{-}1400 \text{ cm}^{-1}$ and a resolution of 4 cm^{-1} , and (v) a low-noise CCD camera (1340×400 pixels). The collection efficiency of the Raman system has been determined to be 2.8%. Except for the laser cooling subsystem, the Raman system fits in a $0.61 \text{ m} \times 0.61 \text{ m} \times 0.61 \text{ m}$ box.

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INTRODUCTION

We have developed a Raman spectroscopy system specifically aimed at rapid and sensitive detection and identification of chemical aerosols. Using an earlier version of this system, we previously reported the Raman detection and identification of isovanillin ($\text{C}_8\text{H}_8\text{O}_3$, CAS No. 621-59-0; Molecular mass 152.15; Density 1.41) aerosol particles of mass concentration M_c of 1.8 ng/cm^3 in a 30 s integration period with a signal-to-noise ratio (SNR) of 19 (Aggarwal et al. 2014). We have dramatically improved this system and in this paper we report the Raman detection of isovanillin aerosol mass concentration M_c of 12 pg/cm^3 in a 15 s integration period with an SNR of 32. The current sensitivity is $> 150\times$ higher than that reported previously. This increase in the detection sensitivity is due to improvements in the laser power, Raman signal collection efficiency, and the incorporation of a virtual impactor aerosol concentrator with a mass concentration factor of about 60.

EXPERIMENTAL

Figure 1 shows an optical schematic of the Raman spectroscopy system.

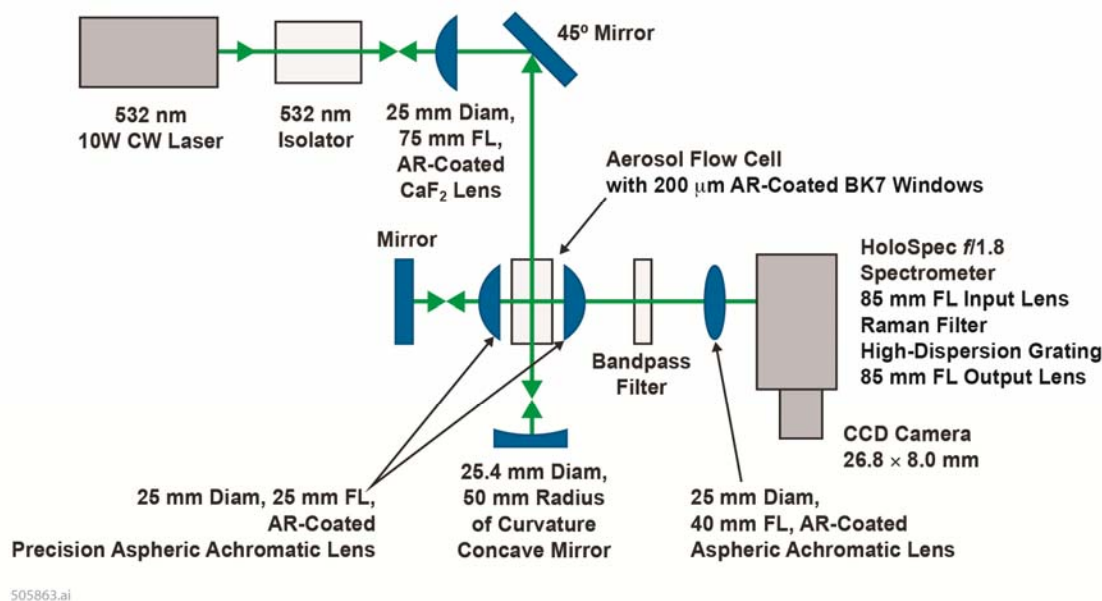


Fig. 1. Schematic of the optical configuration for the Raman spectroscopy system

The major components of the Raman system are:

- (i) 532 nm 10 W cw diode-pumped solid-state laser, which is polarized along the out-of-page direction in Fig. 1.
- (ii) 532 nm optical isolator.
- (iii) Custom-built virtual impactor aerosol concentrator with mass concentration factor of about 60 (Sioutas et al. 1994, Kim et al. 2000, and

Wang et al. 2013). The aerosol concentration is monitored with an optical particle sizer.

- (iv) Aerosol flow cell, fabricated by the U.S. Army Edgewood Chemical and Biological Center (ECBC), with two BK7 windows for the propagation of the laser beam and two BK7 windows for the propagation of the Raman scattered light. These four BK7 windows are attached to the flow cell with epoxy. The diameter of the tube for the aerosol inlet into the flow cell is 3 mm. There is a concentric tube of 5 mm diameter for the sheath flow of HEPA filtered air into the flow cell.
- (v) Concave mirror with 25.4 mm diameter and 50 mm radius of curvature.
- (vi) Bandpass filter with 25 mm diameter.
- (vii) Long wave pass Raman filter with 50 mm diameter.
- (viii) HoloSpec f/1.8 Raman spectrometer model, which is equipped with a high-dispersion grating for the spectral coverage 400-1400 cm^{-1} .
- (ix) CCD camera model with 1340x400 pixels format and operated at a temperature of -75°C .

The diameter of the focal spot inside the flow cell is $50 \pm 5 \mu\text{m}$. The laser beam is double-passed through the focal spot using a concave mirror with 50 mm radius of curvature. Double-sided Raman signal collection is achieved with two f/1.1 collection lenses each 25 mm effective focal length (EFL) and a plane mirror as shown in Fig. 1. The Raman scattered light is collected at approximately 90° to direction of the laser propagation. The f/1.8 lens for focusing the light on the $83\text{-}\mu\text{m}$ slit of the spectrometer has a 40 mm EFL. The spectrometer slit is parallel to the laser propagation direction. The spectral resolution of the Raman system has been determined to be 4 cm^{-1} . The magnification of the image of the laser focal spot on the spectrometer slit is 1.6.

The isovanillin aerosol is generated by a small household blender, which is loaded with isovanillin powder to just above the blender blades. The aerosol generated in the blender flows into a large (20 liter) aerosol chamber after which it passes through a soft X-Ray aerosol particle charge neutralizer before entering the virtual impactor aerosol concentrator and then passes to the aerosol flow cell of the Raman spectroscopy system. The aerosol and sheath flow rates into the flow cell are controlled by two flow controllers. The sheath flow rate is approximately 3x the aerosol flow rate of $\sim 0.05 \text{ LPM}$.

RESULTS AND DISCUSSION

The basic equation for the Raman signal is given by

$$R_s = (\eta_c \eta_q \sigma_R N_m L) \left(\frac{P_L \tau}{h \nu_L} \right) T_s, \quad (1)$$

where η_c is the double-sided collection efficiency, η_q is the quantum efficiency of the CCD camera, σ_R is the Raman cross section, N_m is the molecular concentration in the laser sample volume, L is the length of the laser spot imaged on the CCD, P_L is the double-passed laser power in the focal spot, τ is the integration time for the

measurement, $h\nu_L$ is the laser photon energy, and T_S is the transmittance of the Raman system. The Raman signal does not increase linearly with L because of the vignetting for the off-axis points on the laser focal spot. The Raman signal for L of 3.0 mm is equal to 85% of that expected for no vignetting. The value of the system transmittance T_S is determined to be

$$T_S = \frac{1}{2} \left(1 + T_W^2 T_{CL}^2 R_M \right) T_W T_{CL} T_{BP} T_{FL} T_{IL} T_{RF} G_{DE} T_{OL} = 48\%. \quad (2)$$

where T_W (99%) is the transmittance of the AR-coated BK7 windows on the flow cell, T_{CL} (97%) is the transmittance of the AR-coated signal collection lens, R_M (95%) is the reflectance of the signal collection mirror, T_{BP} (97%) is the transmittance of the bandpass filter, T_{FL} (97%) is the transmittance of the AR-coated focusing lens used for focusing the light on the 83 μm spectrometer slit, T_{IL} (94%) is the transmittance of AR-coated 85 mm EFL f/1.8 input lens of the Raman spectrometer, T_{RF} (99%) is the transmittance of the Raman filter, G_{DE} (65%) is the diffraction efficiency of the high-dispersion grating, and T_{OL} (94%) is the transmittance of the AR-coated 85 mm EFL f/1.4 output lens of the spectrometer used to focus the light on the CCD camera.

The performance of the Raman system is determined by comparing the measured value of R_S for the 1285 cm^{-1} mode of atmospheric CO_2 and the corresponding value calculated from Eq. (1). Figure 2 shows the Raman spectrum of the 1285 cm^{-1} mode of 485 ppm atmospheric CO_2 obtained using a value of 3 mm for L , 17 W for P_L , and 15 s for τ .

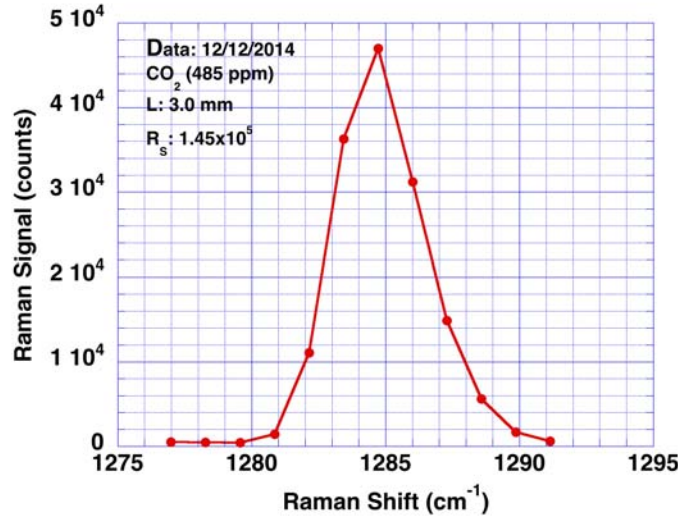


Fig. 2. Raman spectrum of the 1285 cm^{-1} mode of 485 ppm of atmospheric CO_2 obtained using a value of 3 mm for the laser path length L , 17 W for the double-pass laser power P_L , and 15 s for the integration time τ .

The concentration of CO₂ was measured with a CO₂ probe. The measured value of R_S determined from the Raman spectrum of Fig. 2 is equal to 1.45×10^5 counts integrated over the 1280 - 1291 cm⁻¹ spectral bandwidth. The calculated value of R_S obtained from Eq. (1) is $5.17 \times 10^6 \eta_c$ counts using values of 98% for η_q , 4.5×10^{-30} cm² for σ_R (Montero 1983), 1.19×10^{16} /cm³ for N_m corresponding to 485 ppm of CO₂, 0.3 cm for L , 17 W for P_L , 15 s for τ , 3.73×10^{-19} J for $h\nu_L$, and 0.48 for T_S . Using these measured and calculated values of R_S , we obtain a value of 2.8% for the double-sided collection efficiency η_c . The expected value of η_c is 8.5% for f/1.1 collection lenses x 85% signal for the value of 3 mm for L . Thus the measured Raman signal is 1/3 of its expected value. This discrepancy is not understood.

The mass concentration factor of the virtual impactor was measured using its off and on modes of operation. In the off mode, no air is pulled through the major flow port of the concentrator and ~ 0.05 LPM is pulled through the minor flow and into the Raman system flow cell. In the on mode, 3.0 LPM is pulled through the major flow port and ~ 0.05 LPM is pulled through the minor flow port and into the Raman system flow cell. Figure 3 shows the Raman spectra for the 1116 cm⁻¹ mode of isovanillin (Aggarwal et al. 2014). The mass concentration factor C_F (signal-on to signal-off ratio) was determined to be 63.

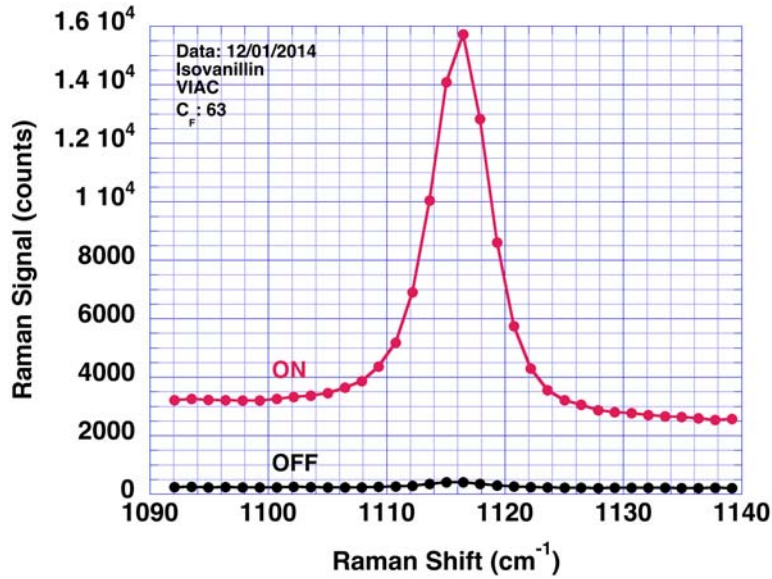


Fig. 3. Raman spectra for the 1116 cm⁻¹ mode of isovanillin aerosol particles obtained using the virtual impactor aerosol concentrator in the off and on positions.

Figure 4 shows the Raman spectrum of the isovanillin aerosol particles obtained with the virtual impactor concentrator. The measured value of the Raman signal for the spectrum of Fig. 4 is $2.90 \pm 0.18 \times 10^3$ counts over the 1104 - 1125 cm⁻¹ spectral bandwidth of the background-corrected signal.

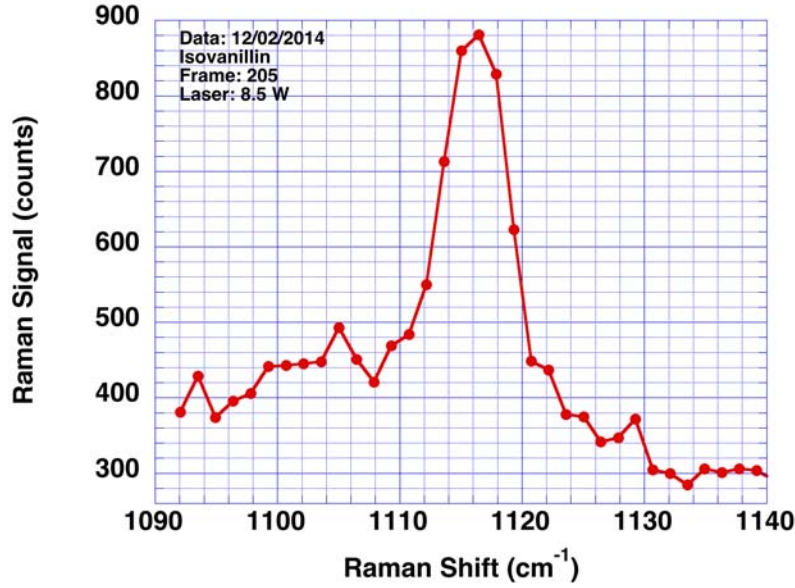


Fig. 4. Raman spectrum of the 1116 cm⁻¹ mode of isovanillin aerosol particles obtained with the virtual impactor aerosol concentrator using 3 mm for L , 17 W for P_L , and 15 s for τ .

The mass concentration of the isovanillin aerosol particles for the Raman spectrum of Fig. 4 is determined from the following equation:

$$M_C = \left(\frac{\sigma_{CO_2}}{\sigma_{iso}} \right) \left(\frac{N_{CO_2}}{R_{CO_2}} \right) \left(\frac{R_{iso}}{C_F} \right) m_{iso}, \quad (3)$$

where σ_{CO_2} is the Raman cross section of the 1285 cm⁻¹ mode of CO₂, σ_{iso} is the Raman cross section of the 1116 cm⁻¹ mode of isovanillin aerosol particles, N_{CO_2} is the molecular concentration of atmospheric CO₂, R_{CO_2} is the Raman signal for the 1285 cm⁻¹ mode of CO₂, R_{iso} is the Raman signal of the isovanillin aerosol particles, and m_{iso} is the mass of the isovanillin molecule. Using values of 4.5x10⁻³⁰ cm² for σ_{CO_2} , 3.3x10⁻²⁸ cm² for σ_{iso} , 1.19x10¹⁶/cm³ for N_{CO_2} corresponding to 485 ppm, 1.58x10⁵ counts for R_{CO_2} , 2.90x10³ for R_{iso} , 63 for C_F , and 2.53x10⁻²² g for m_{iso} , Eq. (3) yields a value of 12 pg/cm³ for M_C , which is in agreement with the value of 12 pg/cm³ as measured by an optical particle sizer (TSI 3330).

The limit of detection (LOD) for the mass concentration of isovanillin aerosol particles for rms signal-to noise ratio of 3 is given by

$$LOD = \left(\frac{3N_{RMS}}{R_{iso}} \right) M_C, \quad (4)$$

where N_{RMS} is the RMS noise of the CCD. Using values of 30 counts for N_{RMS} , 2.90x10³ counts for R_{iso} , and 12 pg/cm³ for M_C for the spectrum of Fig. 5, Eq. (4) yields a value

of 0.37 pg/cm³ in 15 s for LOD, which corresponds to molecular concentration of 1.9x10⁹/cm³.

SUMMARY

We have detected isovanillin aerosol particles of mass concentration of 12pg/cm³ in 15 s using a compact 532 nm 10 W double-pass laser Raman system with double-sided collection and a virtual impactor aerosol particle concentrator with concentration factor of 63. We believe this represents the lowest chemical aerosol concentration and signal integration period product ever reported for a Raman spectroscopy system. The limit of detection (SNR = 3) for isovanillin aerosol particles has been determined to be 0.37 pg/cm³ in 15 s.

Acknowledgments

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